

NIGMS Fluorine Detection

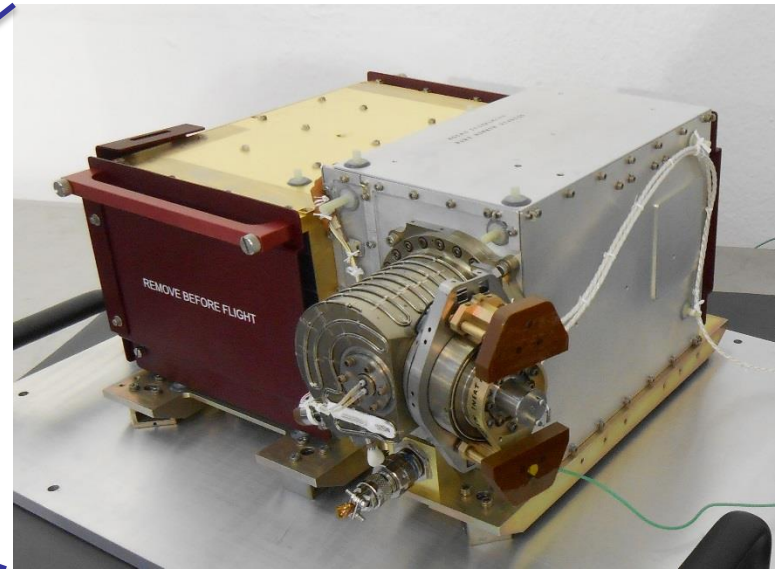
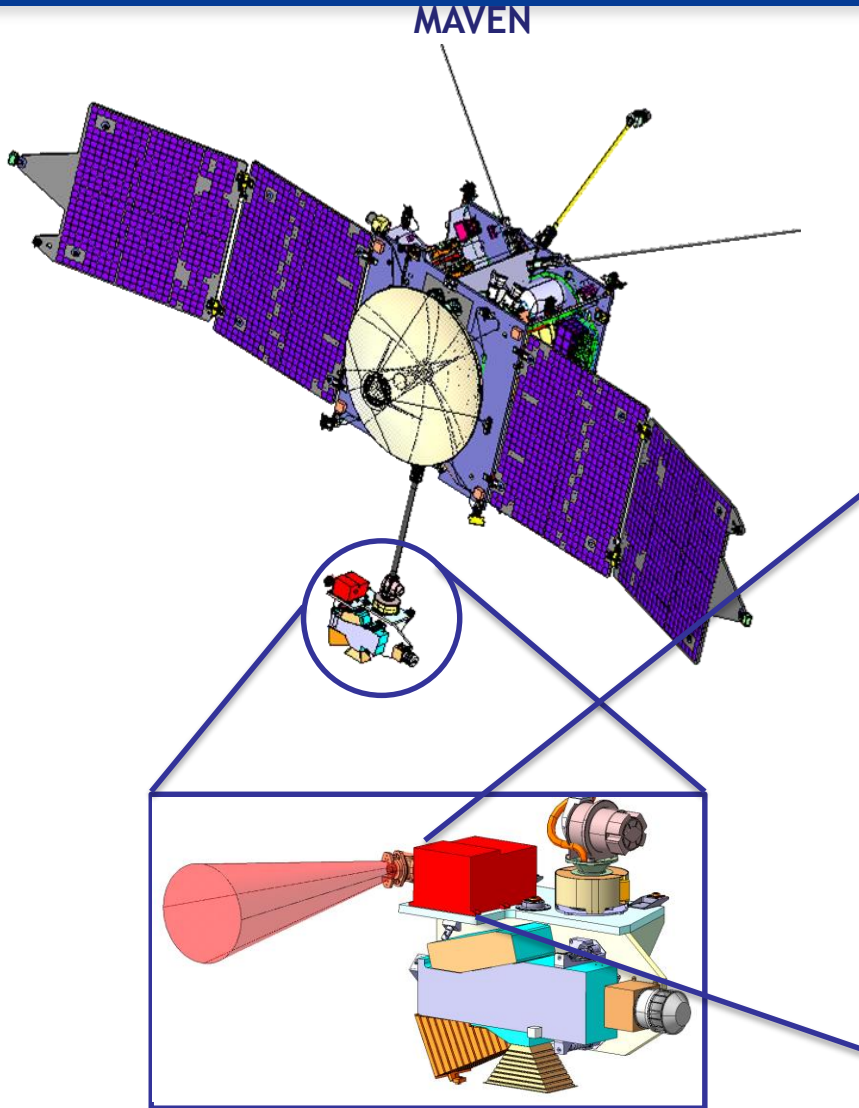
July 31, 2015

Contamination, Coatings, Materials and Planetary
Protection Workshop

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Accommodation on the Spacecraft



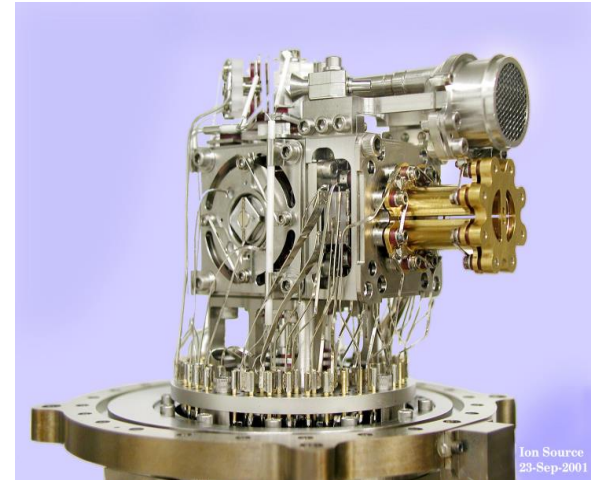
NGIMS Measurement Requirements

NGIMS measurement requirements:

- Profiles of He, N, O, CO, N₂, NO, O₂, Ar, and CO₂ & their major isotopes
 - From the homopause up to one scale height above the exobase (130 km for He, ~12 km for CO₂)
 - Vertical resolution of one half scale height for each species
 - 25% accuracy
- Profiles of thermal O₂⁺, CO₂⁺, NO⁺, O⁺, CO⁺, C⁺, N₂⁺, OH⁺, & N⁺
 - From the ionospheric main peak (~120 km) up to the nominal ionopause (~400 km)
 - Vertical resolution of one half O₂⁺ scale height
 - 25% accuracy.

The combination of NGIMS sampling performance and spacecraft and attitude ad orbit give:

- Required profiles of neutral and ion species
- Neutral temperature from scale height.
- Isotopes: (¹³C/¹²C, ¹⁸O/¹⁶O, ¹⁵N/¹⁴N, ⁴⁰Ar/³⁶Ar, ³⁸Ar/³⁶Ar)

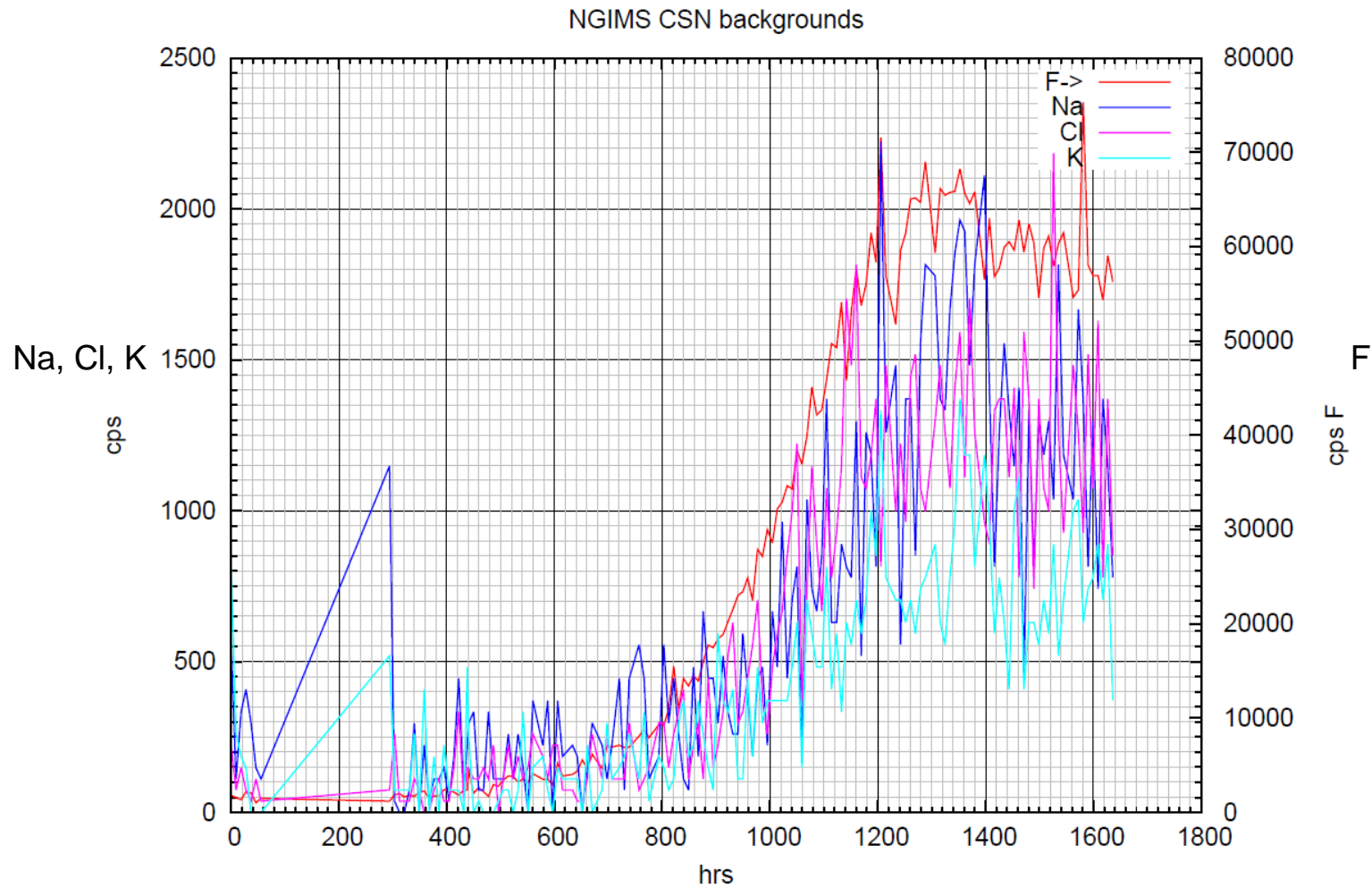


NGIMS Fluorine Signal Increase



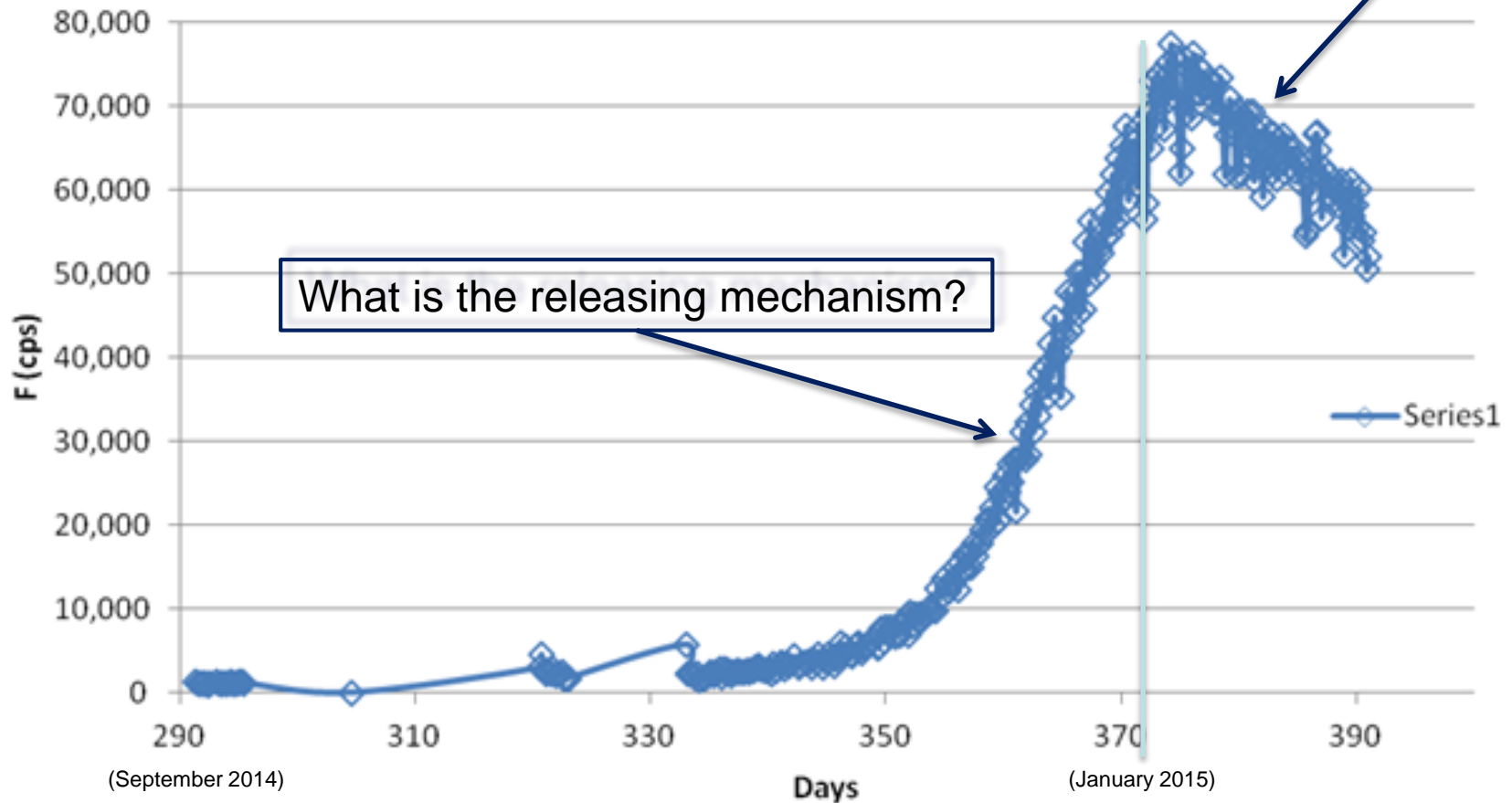
- NGIMS data showed a drift in signal. For example, ratios of open to closed source signal levels or ratios of attenuated to non-attenuated signal levels.
 - There seems to be no issue with the housekeeping data.
 - There is a possibility of contamination issue as we see a corresponding increase in fluorine signal that may be symptomatic of sputtering from MLI on the spacecraft that has a line of sight to the NGIMS.
 - One thought is that with build up of an insulating film we could be seeing some charge build up that is distorting the focusing.

NGIMS Fluorine Signal Increase

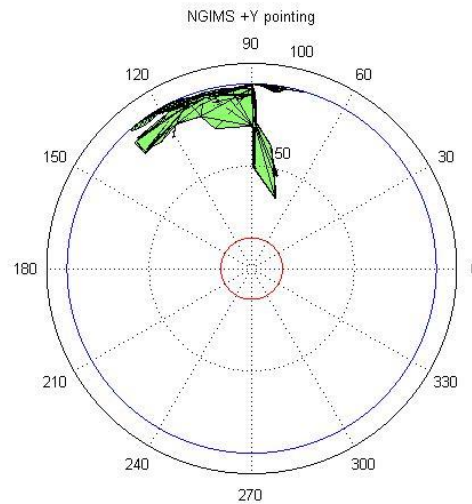
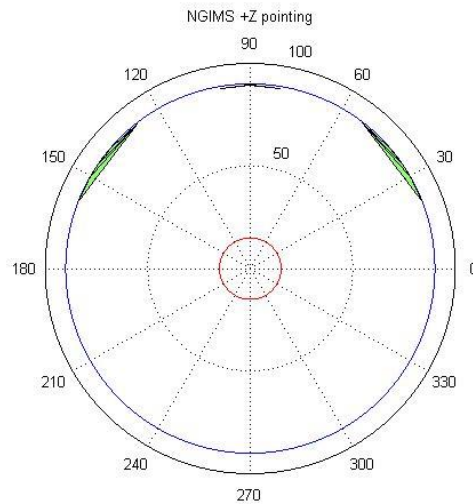


NGIMS Fluorine Detection

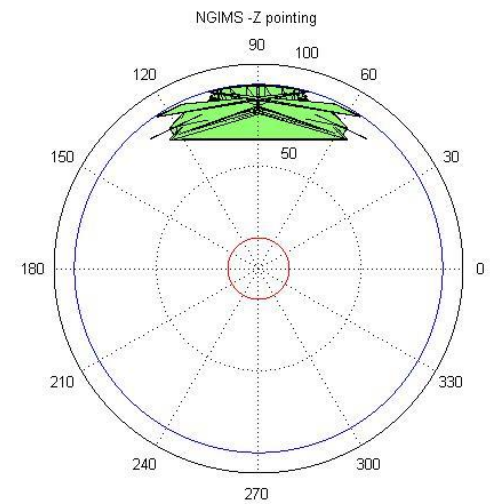
NGIMS CSN Backgrounds



On-orbit NGIMS Field-of-views



90% of time



deep dip

NGIMS Fluorine Signal Increase



- These are elapsed days since 01/01/2013.
 - The profile spans the period of mid Oct 2014 to end of Jan 2015.
- Fluorine counts reached a maximum value around Day 376, then it decreased monotonically.
- A potential explanation of the decay is that the outgassing is seasonal in nature. The periapsis in Dec-Jan was on the night side. I don't know if there is any correlation of this profile with the S/C time spent in the sun light (inducing thermal desorption) or in the fast flows of the magnetosphere (inducing ion sputtering). We should not rule out that this profile is cyclical.
- Guess the fluorine level trend will slow down with time.

- Fluoropolymer wire insulations and their types.
 - DuPont Tefzel ETFE (commonly used wire) could release fluoride ions (often release higher amounts of fluoride)
 - DuPont Teflon PTFE (cannot be melt extruded) insulation could also release fluoride ions
 - DuPont Teflon FEP is very similar in composition to PTFE
- Solar array wire (ETFE)
- Silver Teflon on radiators (FEP)
- Teflon tube, Teflon tape, lacing tape, etc.

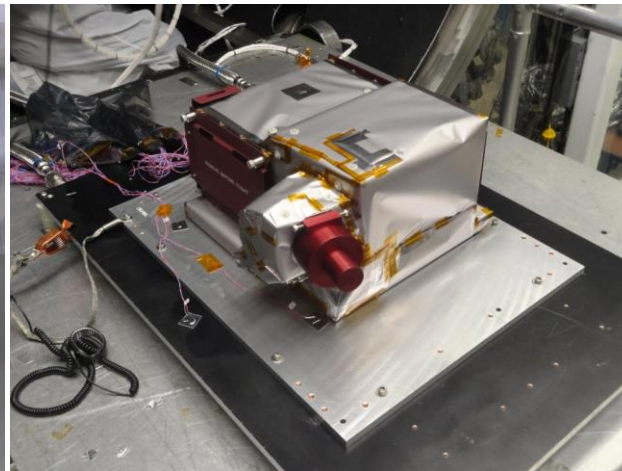
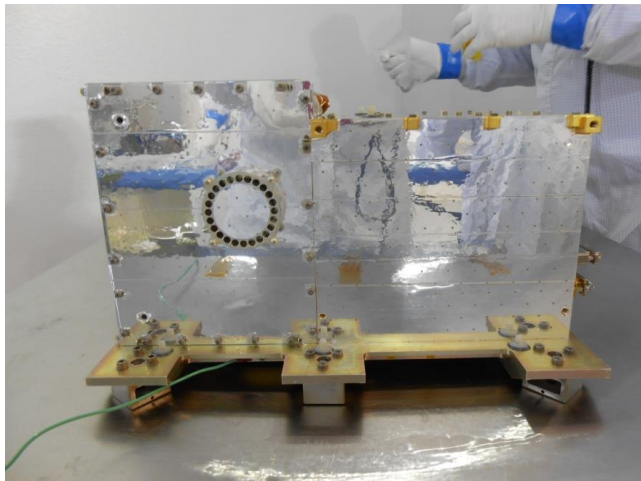
1. ETFE is a copolymer of ethylene and tetraethylene of the formula $[(CF_2-CF_2)_x(CH_2-CH_2)_y]_n$

2. PTFE is a polymer consisting of recurring tetrafluoroethylene monomer units whose formula is $[CF_2-CF_2]_n$

3. FEP resin is a copolymer of tetrafluoroethylene and hexafluoropropylene with the formula $[(CF(CF_3)-CF_2)_x(CF_2-CF_2)_y]_n$

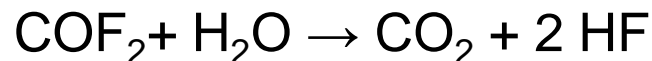
NGIMS Fluorine Sources

- Most fluoropolymer wires are inside NGIMS. There are two small external pigtail wire, but these two exposed wires are out of the instrument field of view
 - No contribution in the direct flux molecular transport.
- ***No fluoropolymer material used inside NGIMS sensor***



- Fluorine may be generated by the following mechanisms
 - Reaction with water
 - Elevated temperature
 - Radiation, atomic oxygen, ultraviolet, spacecraft charging, and vacuum
 - Space environmental synergy

- Differences in manufacturing conditions lead to differences in fluoride released.
 - ETFE insulations have values that are as low as PTFE insulations.
- Carbonyl difluoride (COF_2) released during manufacturing starts the problem.
- COF_2 generation is not contrary to any wire specification requirements.
- Water sources
- Hydrogen Fluoride (HF) is generated



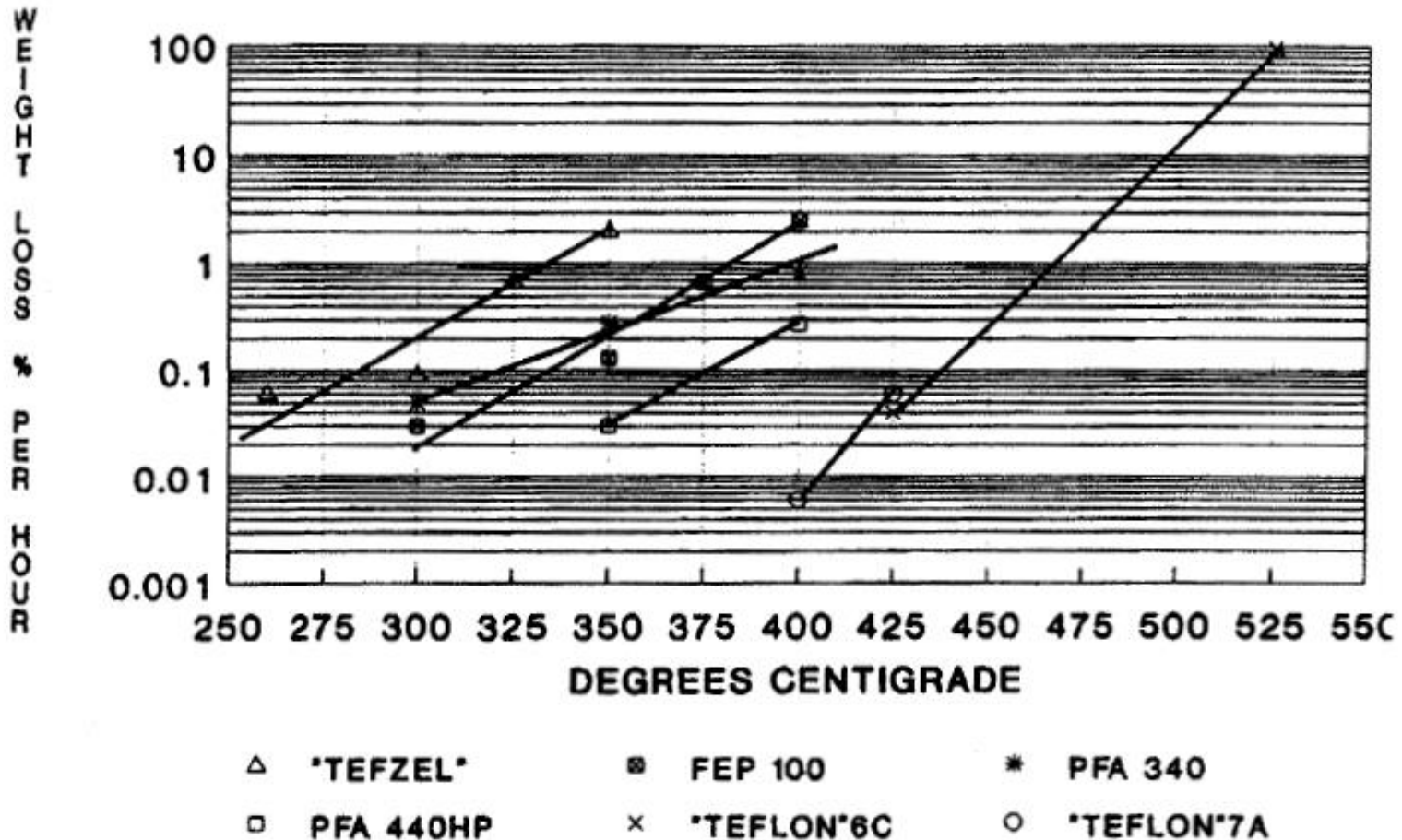
Ref:

1. Aparna Boddapati, "Measurement of Fluoride Generated From Fluoropolymer Wire Insulations"
2. GSFC NASA Advisory (NA-GSFC-2003-03) Some fluoropolymer insulation materials such as Ethylene-Tetrafluoroethylene (ETFE) may outgas trace amounts of fluorine over time.
3. GIDEP alert EA-P-98-02 also cautions about risks of ETFE insulations.

- Fluoropolymers are stable polymers, but they start to decompose slowly when heated to elevated temperatures.
 - Typical melting temperatures/process temperatures are ETFE(220-270°C/310°C), PTFE(330°C/380°C), and FEP(260°C/360°C)
- The four main types of products formed in the decomposition of fluoropolymers are fluoroalkenes, hydrogen fluoride, oxidation products, and low-molecular weight fluoropolymer particulates.

Ref: DuPont, "Guide to the Safe Handling of Fluoropolymer Resins"

Fluoropolymer Resins Weight Loss



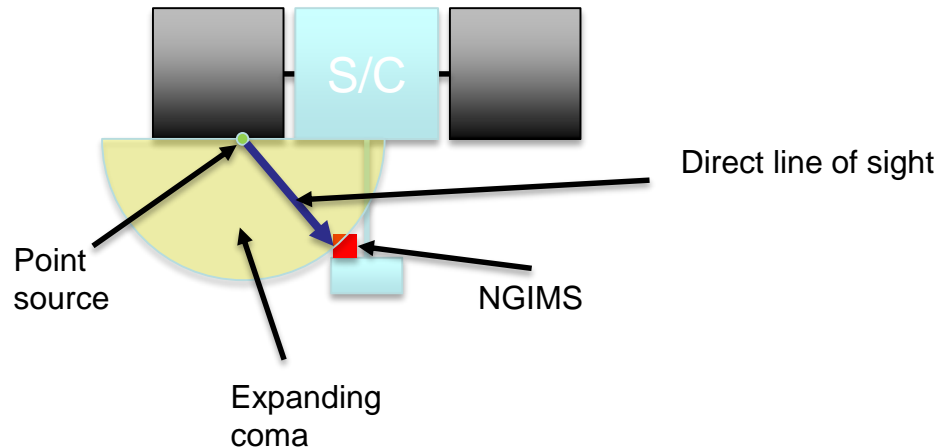
Fluorine Generation Mechanisms



- Thermal cycling, radiation, ultraviolet Radiation
- Atomic oxygen
 - AO erosion of fluoropolymers occurs on low earth orbit, but is less significant on Mars orbit
- Space environmental synergy

- When spacecraft dips into the atmosphere (periapsis segment), back scattering (return flux) of the spacecraft background increases.
 - Back scattered atoms and molecules have a decent chance to be in NGIMS field of view.
- NGIMS detected peak Fluorine counts per second (CPS) was 77,400 CPS which is about 3×10^4 ions/s.
 - Estimated peak fluorine mass is about 2.5×10^{-14} g/s
- Normal direct flux due to spacecraft outgassing flux is 10^{-9} - 10^{-6} g/s, return flux is about 10^{-4} of the direct flux (at LEO).
 - Estimated lower return flux is about 10^{-13} g/s.
 - Electrostatic return?

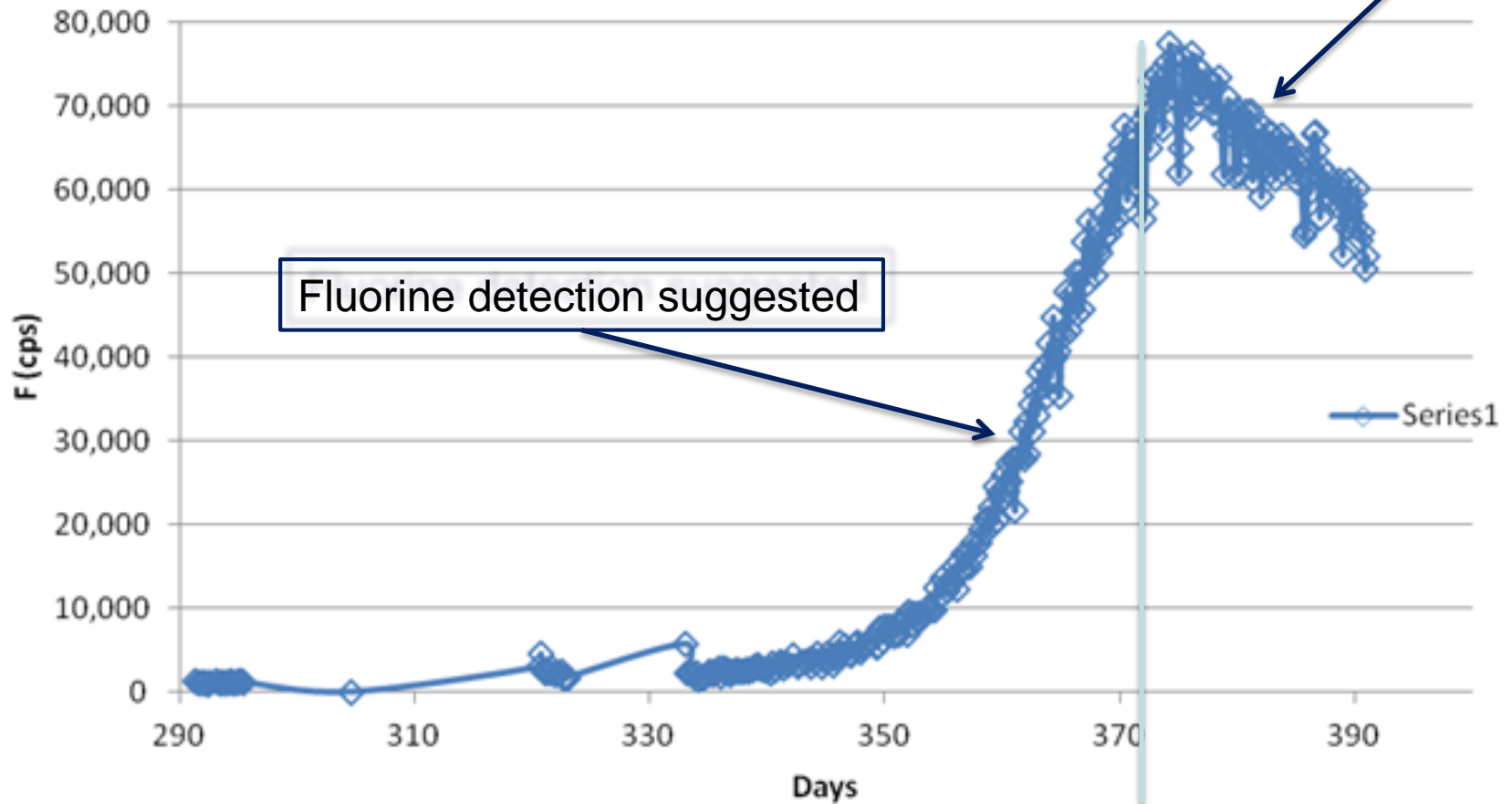
Source rate calculation



- We assume that fluorine is adsorbed on all internal surface of the instrument ($S = 1000 \text{ cm}^2$), and that $1/5$ of the 250uA electron emission is responsible for the sputtering (3×10^{14} electrons/s) over the 1 cm^2 area. The electron-stimulated desorption Yield $Y_i = 3 \times 10^4 / 3 \times 10^{14} = 10^{-10}$. Assuming that this yield of ion is 100 lower than the one for neutrals, the adsorbate coverage $\sim 10^7 \text{ part/cm}^2$
- The total adsorbed fluorine $N_F = 10^7 \times 10^3 = 10^{10}$ particles.
- The fluorine signal was increasing at a rate of 2% per day when it peaked \rightarrow contamination rate $R_F = 10^{10} \times 0.02 / (24 \times 3600) \sim 2300 \text{ part/s}$.
- We assume that the incidence angle of flux of contaminant $= 60^\circ$ with a sensor aperture and vent area $A = 10 \times 0.2 \text{ cm}^2$. The contaminant flux $F_F = R_F / (A \times \cos(60)) = 2300 \text{ part/cm}^2/\text{s}$.
- Assuming a hemispherical emission and a Source-NGIMS distance $= 2.5 \text{ m} \rightarrow$ Source rate $= 2 \times \pi \times r^2 \times F_F = 9 \times 10^8 \text{ part/s} = 3 \times 10^{-14} \text{ g/s}$

NGIMS Fluorine Detection

NGIMS CSN Backgrounds



Summary



- NGIMS is a very sensitive mass spectrometer.
- NGIMS could detect released fluorine by back scattering transport mechanism.
- Fluorine level is stabilized at 40,000 cps.